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A NEW CLASS OF CHEMICAL SENSORS FOR GASES BASED ON
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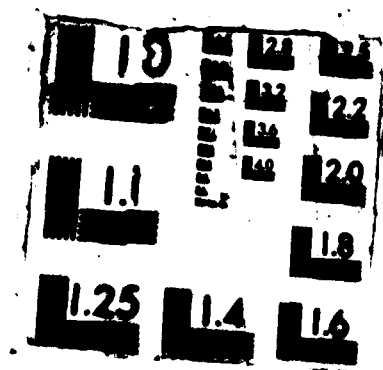
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A New Class of Chemical Sensors for Gases Based on
Photoluminescence from Semiconductor-Derived Interfaces

by

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A NEW CLASS OF CHEMICAL SENSORS FOR GASES BASED ON
PHOTOLUMINESCENCE FROM SEMICONDUCTOR-DERIVED INTERFACES

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ABSTRACT

The photoluminescence (PL) of semiconductors can be perturbed by exposure of the solid to gases. These physicochemical interactions occurring at the semiconductor surface can be exploited to create a new class of chemical sensors. For homogeneous semiconductors, a dead-layer model has been used to correlate changes in PL intensity with variations in the depletion width W caused by the gas. A graded $n\text{-CdS}_x\text{Se}_{1-x}$ substrate permits modulation of the PL spectral distribution by gases and is color-coded to permit PL changes to be correlated with variations in the effective electric field present in the solid. Three structures illustrate these PL effects: Pd-coated semiconductors can respond to hydrogen gas; semiconductors that have been chemically derivatized with ferrocene can sense volatile oxidants and reductants; and etched semiconductors can respond to sulfur dioxide and ammonia, presumably through acid-base interactions. All of the structures lend themselves to device fabrication by use of optical fiber technology.

INTRODUCTION

The intense interest in chemical sensing has prompted a search for new strategies and techniques (1). We have observed that the bulk photoluminescence (PL) of semiconductors can be influenced by chemistry occurring at the surface of the solid, suggesting the use of this effect for chemical sensing (2,3). In this paper we summarize our past work related to sensing and describe recent results that expand the scope of gas detection.

For homogeneous semiconductors, the PL spectral distribution is essentially unaffected by surface chemistry, and we have employed a dead-layer model (4) to correlate changes in PL intensity with changes in the depletion width W of the solid. The dead-layer model assumes that the region of the semiconductor that supports the electric field is nonemissive, because electron-hole (e^-h^+) pairs

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that are formed in that region are separated so rapidly that they are unable to radiatively recombine.

A quantitative expression for the dead-layer model is given in eq. 1, and its derivation, based on Beer's Law, is illustrated in Figure 1. In the equation, PL_1 and PL_2 are the PL intensities for

$$PL_1/PL_2 = \exp(-\alpha' \Delta D) \quad (1)$$

the two chemical states of the sensor, wherein the semiconductor is in depletion; $\alpha' = (\alpha + \beta)$, where α and β are the absorptivities of the semiconductor for the exciting light and emitted light, respectively; and ΔD is the change in dead-layer thickness, equated herein with the change in W . An operational test of the dead-layer model involves measuring the PL intensity ratio for several interrogating excitation wavelengths for which the solid has different absorptivities. A value for ΔD should be obtained from eq. 1 that is independent of excitation wavelength.

Mattler has shown that a more sophisticated analysis of PL, consisting of plots of PL intensity vs. optical penetration depth, can simultaneously yield the absolute value of W as well as the surface recombination velocity S , which can also influence PL intensity (5). Implicit in our use of eq. 1 is the notion that S either does not vary between states 1 and 2 or that it is relatively large ($S \gg L/\tau$ and $\alpha L^2/\tau$, where L and τ are the diffusion length and lifetime of the minority carrier, respectively) (6).

The use of spatially inhomogeneous semiconductors provides a means for modulating the spectral distribution or color of PL. Our prototypical sample for demonstrating these effects is a graded $n\text{-CdS}_x\text{Se}_{1-x}$ substrate. Prepared by the vapor-phase diffusion of S into single-crystal $n\text{-CdSe}$, the solid's PL is color-coded to identify the spatial origin of e^-h^+ pair recombination, since the PL band maximum in $\text{CdS}_x\text{Se}_{1-x}$ alloy compositions varies with composition, as shown in eq. 2 (7-10). The depth of these various compositions from

$$\lambda_{\text{max}} (\text{nm}) = 718 - 210 X \quad (2)$$

the surface is determined by Auger electron spectroscopy (AES) with Ar^+ sputter etching; typically, the overall thickness of the graded zone is about one micron. The presence of different compositions gives rise to an effective electric field (EEF) in these solids, containing contributions from, for example, band-edge and effective-mass gradients. The affected portion of the PL spectrum identifies, using eq. 2 and the AES data, the depth to which the EEF is altered by chemistry occurring at the surface.

Although PL is a bulk property, the fact that it is influenced by the presence of an electric field suggested that surface chemistry could affect the emission. Since the depletion width W arises from a mismatch in chemical potentials between the semiconductor and the phase in contact with it, a chemical reaction that strongly affects the chemical potential of the contacting phase should perturb the PL signal. Alternatively, chemistry that affects the surface recombination velocity S can influence PL.

In sections below we describe three systems that illustrate these concepts. The first two, a semiconductor coated with Pd that senses hydrogen and a derivatized semiconductor that senses volatile oxidants and reductants, have been described and are updated. The third system is prepared by simple chemical etching and shows strong PL changes when exposed to sulfur dioxide and ammonia gases.

EXPERIMENTAL

Techniques used for preparing Pd-coated and ferrocene-derivatized samples have been described (2,3,11). Single-crystal c -plates ($10 \times 10 \times 1$ mm) of n -type CdSe were obtained from Cleveland Crystals, Cleveland, Ohio. The crystals were vapor-grown with resistivities of ~ 2 ohm-cm. After being cut to dimensions of ~ 0.25 cm² \times 1 mm, the samples were etched in Br₂/MeOH (1:30 v/v), ultrasonically cleaned in MeOH, and suspended by an edge with DUCO cement from a glass rod. The rod was then placed in an adapter that served as a stopper for a 20-mm diameter glass tube that encircled the semiconductor. Two diametrically opposed stopcocks near the bottom of the tube and below the semiconductor served as gas inlets for nitrogen (Matheson; 99.99%) and nitrogen mixed with either sulfur dioxide (Matheson; 99.98%) or ammonia (Matheson; 99.99%); a stopcock near the top of the tube and above the semiconductor served as the gas exit and was connected to a flowmeter that was vented into a hood. Experiments were thus done at atmospheric pressure at flow rates of ~ 100 mL/min. Connections were made with glass tubing and Tygon joints. Sample excitation was accomplished with the 457.9 and 514.5 nm lines of a Coherent Radiation CR-12 Ar⁺ laser and the 632.8 nm line of a Melles-Griot 10 mW He-Ne laser, using Corning 2-58 and interference filters. Incident intensities were typically ~ 1 mW/cm². PL was detected by placing an optical fiber near the emitting surface of the semiconductor and feeding the light into a McPherson 0.3-m monochromator, equipped with a photon counting detection system. Graded n -CdS _{x} Se _{$1-x$} samples were prepared as previously described (8).

RESULTS AND DISCUSSION

Hydrogen sensing with palladium-coated semiconductors. When a thin layer of Pd (~ 100 Å) is sputtered onto a single-crystal n -CdS

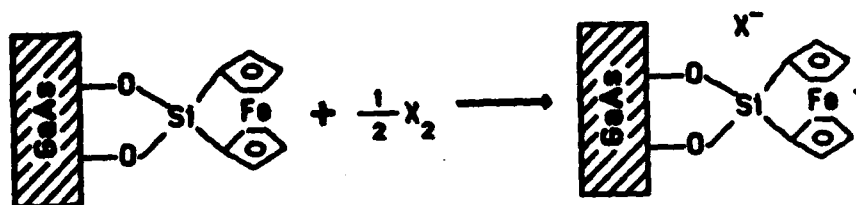
substrate to form a Schottky barrier, the band edge PL of the substrate increases when the ambient gas is changed from N_2 to a 3:1 $N_2:H_2$ mixture (2). Qualitatively, the enhancement is consistent with a reduction in W in the hydrogen ambient. Quantitatively, the data fit a dead-layer model (eq. 1). A typical enhancement of 70% corresponded to a reduction in W of nearly 600 Å. Connection of electrical leads to the Pd and CdS surfaces produces a Schottky diode whose current-voltage (i-V) properties permit extraction of the Schottky barrier heights in the two gaseous ambients. Our samples typically exhibited a reduction in barrier height from 0.6 to 0.4 eV in passing from air to hydrogen, the latter value being obtained from both i-V and PL data. Control experiments indicated that the effects observed did not arise from either optical properties of the Pd film or thermal effects. The PL increase could be reversed by exposure to N_2 and then to air; ten reproducible cycles of PL changes were obtained in this way.

Color modulation was demonstrated using Pd-coated, graded n-CdS_xSe_{1-x} samples (2). Exposure to H_2 caused PL enhancements of up to 50% for wavelengths between 500 and 600 nm. The latter wavelength corresponds to PL from an approximately CdS_{0.5}Se_{0.5} composition, which, from AES data, lay ~0.1 microns from the surface. Thus the EEF in this solid could be altered to roughly this depth.

The origin of these effects has been attributed to a lowering of the Pd work function as a result of the dissolution of hydrogen in the metal, reducing the Schottky barrier (12). A description of the barrier height reduction in terms of the surface-dipole component of the metal work function has also been proposed (13).

In more recent studies, we were able to sense H_2 through similar PL intensity enhancements using n-type, Al-doped ZnSe and Te-doped CdS as substrates; for both of these materials subband gap PL was monitored (11). With CdS as the substrate, we also compared D_2 and H_2 for PL response. Although the final enhancements for the two gases were the same within experimental error, the D_2 response was considerably more sluggish.

Derivatized surfaces as sensors for volatile oxidants and reductants. The covalent bonding of a redox-active film to the surface of a semiconductor provides a second structure for sensing. We thought that the idealized structure sketched below, prepared from an etched n-GaAs surface and a ferrocene derivative (3,14), would yield a change in PL intensity upon oxidation, since the chemical potential of the film would be altered. Indeed, exposure of the derivatized surface to gaseous I_2 or dry Br_2 in a stream of N_2 causes the band edge PL intensity of the GaAs substrate to be quenched. The changes fit a dead-layer model, with W increasing by



about 250 Å upon exposure to I_2 . That oxidation has taken place was verified by cyclic voltammetry in CH_3CN (0.1 M $[\text{n-Bu}_4\text{N}]\text{BF}_4$ as supporting electrolyte); this technique also showed that the film only possessed a few monolayers of redox-active material. Alternatively, oxidation could be verified by using the structure to sense a volatile reductant: exposure to gaseous N_2H_4 restored the initial PL signal. These spectral changes could be maintained over 10 cycles of alternate exposure to I_2 and N_2H_4 .

In more recent work, we have examined changes in both W and S with film oxidation, using plots of PL intensity vs. optical penetration depth (vide supra) (11). This contactless method of analysis indicates that S is large ($\sim 10^5$ cm/s) and unaffected, within experimental error, by film oxidation with iodine, thus justifying the use of the dead-layer model on this structure.

Other substrates have been employed for observing PL changes (11). The use of ferrocene-derivatized n-GaAs_{0.6}P_{0.4} leads to changes in PL intensity at ~ 650 nm that are reversible with N_2H_4 . And derivatization of the graded n-CdS_xSe_{1-x} substrate produces a modest color change, resulting from the quenching of near-surface PL contributions by exposure to I_2 ; these changes, too, are reversible with N_2H_4 .

A noteworthy observation we have made for these systems is that prolonged exposure to an oxidant may cleave some of the bonds that anchor the redox-active species to the semiconductor: cyclic voltammograms of derivatized n-GaAs samples obtained after exposure to greater than stoichiometric amounts of I_2 vapor reveal a drastically diminished electrochemical signal. While this could restrict solution sensing, it is less of a concern for gaseous chemical sensing, since in the absence of a solvent even a cleaved redox-active species remains proximate to the surface.

Etched semiconductor surfaces as sensors. The PL from single crystals of n-CdSe that have been etched with Br_2/MeOH and exposed to air exhibits a surprising sensitivity to SO_2 and NH_3 . Figure 2 reveals that exposure to a flow of pure SO_2 gas quenches the 720 nm PL intensity of CdSe relative to its intensity in N_2 . The effect is reasonably reversible, as shown in the figure, but often requires

a "conditioning" period, during which the intensities in N_2 and SO_2 move considerably from their initial values. Table I shows that the PL changes fit the dead-layer model: for one particularly responsive sample, an expansion in W (ΔD) of about 600 Å is observed in passing from N_2 to pure SO_2 . It is worth emphasizing that in attributing all of the change in PL to a change in W , we are assuming that S is either invariant or relatively large in the two gaseous ambients.

In contrast to the SO_2 results, exposure to NH_3 causes a substantial enhancement in PL intensity relative to the intensity in N_2 . Figure 3 presents a set of responses to different partial pressures of NH_3 ; in each case N_2 serves as a carrier gas, yielding a total pressure of 1 atm. A squarish response is seen except when pure NH_3 is used, when a large transient gives way to a smaller final increase. The PL data in pure NH_3 (after the signal stabilized) were found to obey the dead-layer model; Table I shows that for one sample W contracted by about 700 Å in passing from N_2 to NH_3 .

From the data in Figure 3 and analogous experiments for SO_2 , working response curves can be generated for the two gases, as shown in Figure 4. Although the sensitivity is modest, both gases can be detected at partial pressures of $\sim 10^{-3}$ atm. Also shown on the figure is the insensitivity of PL to a variety of gases. We found that N_2 , Ar, CO, CO_2 , H_2 , and N_2O yielded indistinguishable PL signals.

In preliminary experiments, we have seen analogous PL changes with etched, homogeneous CdS_xSe_{1-x} substrates, indicating that the graded $n-CdS_xSe_{1-x}$ substrates should deliver a change in spectral distribution relative to N_2 gas with exposure to NH_3 and SO_2 gases. Figure 5 demonstrates this effect for SO_2 gas: the near-surface PL arising from S-rich compositions is preferentially quenched. Enhancement over a comparable spectral region is observed if NH_3 is introduced.

In analyzing these PL changes we were concerned initially with thermal effects. We do not believe that these play a very important role for two reasons. First, at the low incident powers employed (~ 1 mW/cm²) and with the convective cooling supplied by our substantial gas flow rates (~ 100 mL/min), the sample should remain near ambient temperature. Second, there seems to be no correlation between gaseous thermal conductivities and PL response: the thermal conductivities of NH_3 , CO, and N_2 are similar while those of SO_2 and CO_2 are smaller, and that of H_2 is an order of magnitude larger (15). We emphasize, too, that in many of our experiments we see substantial PL changes even when only small quantities of SO_2 or NH_3 are mixed into the N_2 gas stream.

We believe that the PL changes observed with SO_2 , a Lewis acid, and NH_3 , a Lewis base, and the insensitivity of PL to such molecules as H_2 , Ar, N_2O , CO, and CO_2 , whose acid-base character is

generally less pronounced, suggest that the observed effects may arise from acid-base interactions. These are "dirty" surfaces. If, for CdSe, we presume the surface to be comprised of Cd, Se, O, and H atoms, the opportunities for Lewis acid/base interactions abound. We can envision SO₂ and NH₃ preferring different sites on the surface, resulting in a very different PL response. A greater variety of gas-solid interactions will have to be examined, however, before a stronger case for this kind of interaction can be made.

CONCLUSION

The experiments described herein demonstrate that the bulk PL of a semiconductor can be influenced by chemistry occurring at the surface of the solid, providing a viable means for sensing certain gases. An actual device can be assembled by using a bifurcated optical fiber: the sensor, placed at the fiber junction, can be irradiated using one leg of the fiber and PL, suitably filtered from the exciting light, detected at the other leg of the fiber.

Although the detection of specific gases has been described, these should be regarded as proof-of-concept experiments. In principle, it should be possible to prepare a semiconductor surface, by etching or coating it, so that a desired species can be detected. There is also no reason in principle why the technique cannot be extended to sensing solution species.

Finally, we note the potential of this technique for exploring the steric and electronic landscape of semiconductor-derived interfaces. This is a contactless, in situ method for probing the terrain of these important interfaces.

ACKNOWLEDGMENT

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Table I. Dead-Layer Analysis of n-CdSe PL Properties.^a

Gas	α^{-1} , Å ^b	PL _{gas} /PL _{nitrogen} ^c	ΔD , Å ^d
NH ₃	560	4.1	-730
	1500	1.7	-690
SO ₂	560	0.29	+640
	710	0.39	+610
	1500	0.64	+580

a. Analysis of changes in band edge PL intensity of an n-CdSe sample that has been etched in Br₂/MeOH and exposed to various gases, as described in the Experimental Section.

b. Optical penetration depth of the exciting wavelength, taken as the reciprocal of the absorptivity. Values of α for n-CdSe were taken from: R.B. Parsons, W. Wardzynski, and A.D. Yoffe, Proc. R. Soc. London, Ser. A, 262, 120 (1961). The reciprocal absorptivities of 560, 710, and 1500 Å correspond to the laser excitation wavelengths 457.9, 514.5, and 632.8 nm, respectively.

c. Ratio of PL intensity in the indicated gas to that in nitrogen, both at a pressure of 1 atm.

d. Change in dead-layer thickness in passing from nitrogen to the indicated gas, calculated using eq. 1; an absorptivity of 1.2×10^4 cm⁻¹ (β) was used to correct for self-absorption. Negative values represent a contraction, positive numbers an expansion.

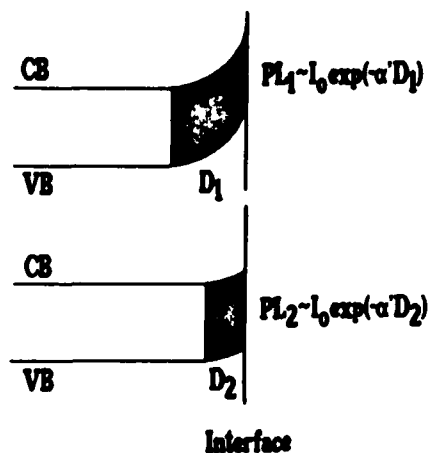


Figure 1. The dead-layer model for analyzing changes in photoluminescence (PL) intensity for two states, 1 and 2. The symbols CB and VB represent the solid's conduction and valence band edges, respectively. For each state, the PL intensity is proportional to the amount of incident light (intensity I_0 ; absorptivity α') absorbed beyond the nonemissive layer whose thickness is D . The ratio of the two PL intensities leads to eq. 1.

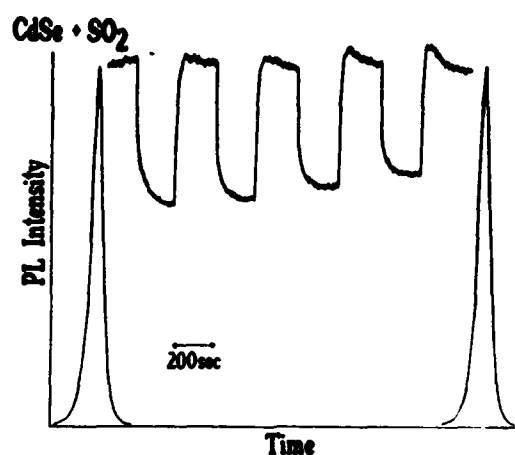


Figure 2. Changes in PL intensity at 720 nm resulting from alternating exposure of an etched n-CdSe sample to N_2 (initial response) and SO_2 . Superimposed on the plot are the original and final PL spectra obtained in N_2 (maxima at 720 nm). Flow rates for both gases were 100 mL/min at 1 atm pressure. The sample was excited using 457.9 nm light.

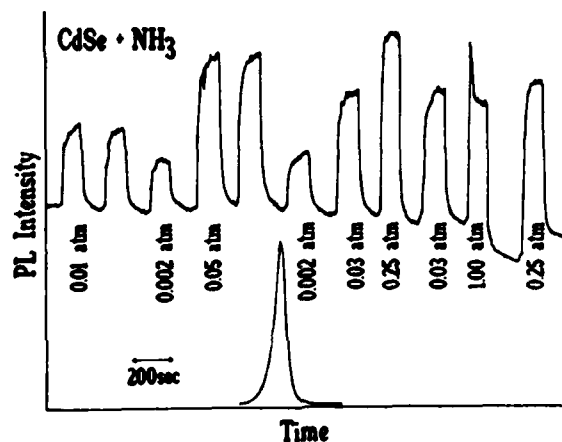


Figure 3. Changes in PL intensity at 720 nm resulting from alternating exposure of an etched n-CdSe sample to N_2 (initial response) and various partial pressures of NH_3 in a N_2/NH_3 mixed flow. The partial pressures of NH_3 are placed beneath the corresponding PL enhancement. Superimposed on the plot is a PL spectrum obtained in N_2 (maximum at 720 nm). Flow rates were 100 mL/min at 1 atm total pressure. The sample was excited using 457.9 nm light.

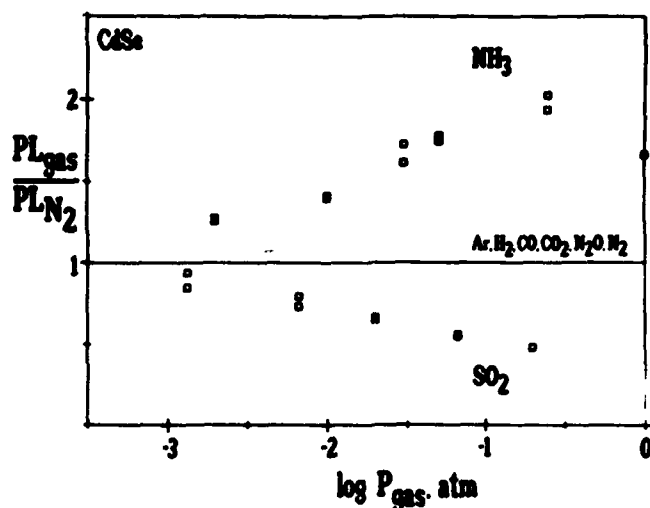


Figure 4. PL response of an etched n-CdSe sample to SO_2 and NH_3 relative to N_2 as a function of the partial pressure of the gas in a N_2/SO_2 or N_2/NH_3 mixture. Flow rates of 100 mL/min were used in all experiments. Other gases that gave the same response as N_2 are indicated in the figure. The sample was excited using 457.9 nm light.

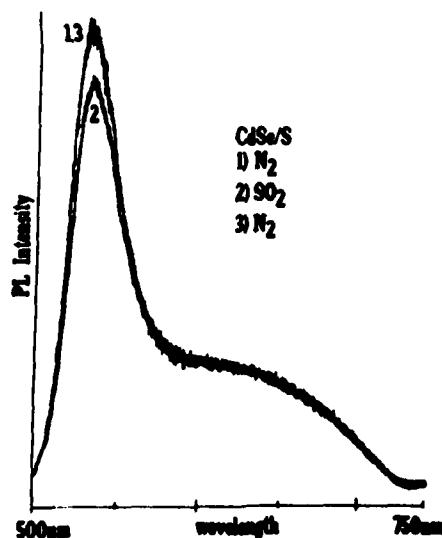


Figure 5. Changes in PL intensity resulting from exposure of a graded n- $\text{CdS}_x\text{Se}_{1-x}$ sample first to N_2 (curve 1), then to SO_2 (curve 2), and finally to N_2 again (curve 3). The sample was excited using 457.9 nm light.

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